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REMOTE ATMOSPHERIC MEASUREMENTS OF CH_4 USING A $LiNbO_3$ TUNABLE SOURCE

ROBERT L. BYER
MARTIN ENDEMANN
EDWARD L. GINZTON LABORATORY OF PHYSICS
STANFORD UNIVERSITY
STANFORD, CA 94305

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A laser transmitter tuned by means of a lithium niobate optical parametric oscillator was employed to demonstrate the capability for remote measurement of gaseous pollutants in the atmosphere. Measurements of methane were obtained continuously over an 18-hour period with a precision of better than 0.06 parts per million. The long path measurements of methane were in excellent agreement with a Bay Area Pollution Control District point monitoring station. Capabilities of the tunable laser transmitter to measure other molecules, as well as atmospheric temperature, are discussed.

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PREFACE

This study was jointly funded by the HQ AFESC Engineering and Services Laboratory and the Environmental Protection Agency's Environmental Sciences Research Laboratory (EPA/ESRL), Research Triangle Park NC 27711. The work was conducted under EPA grant # R-805750-01. The EPA project officer was Dr. William F. Herget, Chief of the Special Techniques Group at ESRL. The study was performed by Dr. Robert L. Byer and Martin Endemann of the Edward L. Ginzton Laboratory of Physics, Stanford University, Stanford CA 94305.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This final technical report has been reviewed and is approved for publication.

HARVEY J. CLEWELL III, Capt, USAF, BSC
Project Officer

MICHAEL G. MacNAUGHTON, Lt Col, USAF, BSC
Chief, Environmental Sciences Branch

EMIL C. FREIN, Lt Col, USAF
Chief, Environics Division

FRANCIS B. CROWLEY, III, Colonel, USAF
Director, Engineering and Services Laboratory

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SECTION I

INTRODUCTION

In 1973 Byer and Garbuny (Reference 1) theoretically analyzed remote atmospheric pollutant monitoring by absorption. Two methods considered were long path absorption measurements using topographical targets and depth resolved absorption measurements using Mie scattering in the atmosphere as a distributed reflector.

Progress in remote monitoring since that first theoretical study has been delayed due to the slow development of tunable laser sources. Depth resolved absorption measurements referred to by the acronym DIAL-LIDAR have now been demonstrated in the visible, ultraviolet and infrared spectral ranges. The progress in remote measurements in tunable source LIDAR has been reviewed, (References 2 and 3) and this method is presently accepted as the primary measurement approach for long range atmospheric measurements using laser sources.

An early research effort at Stanford was to invent and develop a high power tunable source for remote monitoring applications. Under National Science Foundation (NSF) support a tunable infrared source based on a Nd:YAG-pumped $LiNbO_3$ Optical Parametric Oscillator (OPO) was devised and demonstrated. The early device demonstrated a tuning range from 1.4 to 4.0 microns with a linewidth of 4 wavenumbers at an output energy of 10 millijoules per pulse at 10 Hertz.

The wide infrared tuning range and all solid-state construction of the tunable source showed promise for use in infrared remote monitoring. The solid state construction had a potential for reliable operation, and the wide infrared tuning range included molecular absorption bands of a wide variety of pollutant molecules. An additional benefit of the infrared source was eye-safe operation under either daylight or nighttime operations.

The OPO tunable source was used for remote measurements at Stanford in 1977-1978. The Stanford remote monitoring system, which includes a 16 inch diameter receiving telescope, minicomputer and Nd:YAG laser source was designed and constructed under NSF and Electric Power Research Institute (EPRI) support. The early measurements of SO_2 and CH_4 by Baumgartner and Byer (References 4 and 5) were conducted as a demonstration of the measurement potential of the system.

Following the early measurements, an extensive program of research on the OPO source and an optical parametric amplifier (OPA) for increased energy output was carried out. This program led to significant improvements in the tunable source energy, linewidth control, and automatic computer control (References 6

and 7). It also led to a design which demonstrated long term reliable operation under full automatic computer control. The improved OPO/OPA source was used as a transmitter in the present system.

Single-ended remote atmospheric measurements require considerable transmitted energy. For example, measurements using topographical targets typically require 0.01 to 0.1 joules per pulse transmitted energy. For DIAL-LIDAR measurements the required energy increases to near 0.1 to 1.0 joules due to the weak return signal. Future remote monitoring progress requires increased tunable laser capability.

Independent research has been carried out at Stanford to investigate new approaches to high pulse energy tunable infrared sources. The results show good potential for transmitted sources based on Nd:Glass and on pressure tunable CO_2 followed by Raman shifting. These future high energy sources make the potential for depth resolved infrared LIDAR appear particularly good.

The measurement program described in this report illustrates the advantages of the LIDAR approach for remote monitoring. These advantages include rapid measurement time, path averaged measurements, multiple pollutant capability, and excellent measurement precision. The measurement capability will improve as new higher energy sources become available.

SECTION II

DESCRIPTION OF THE MONITORING SYSTEM

The current monitoring system is a derivative of the one reported earlier by Baumgartner and Byer (References 4 and 5). Although the basic set-up remained the same, many essential changes have been made to increase the reliability of the system.

Figure 1 shows a schematic of the present set-up. The pump source for the Optical Parametric Oscillator (OPO) and the Optical Parametric Amplifier (OPA) is an unstable resonator Nd:YAG laser. However, to prevent damage to the $LiNbO_3$ crystals in the OPO and OPA, two important changes were made. First, the cavity length of the Nd:YAG laser was doubled to 1.50 meters to increase the pulse length to 18 nanoseconds and so to decrease the peak optical intensity. This avoids the danger of crystal tracking due to self-focusing effects. The second change was the introduction of a far-field converter, which transforms the doughnut-shaped near-field laser output beam into an Airy-disk profile, which ensures better beam homogeneity. This, in turn, lowers the threshold of the OPO and also avoids hot spots in the beam profile and thus reduces the chance of crystal surface damage.

Extensive studies by Brosnan and Byer lead to improvements of the OPO itself (Reference 6). The introduction of a 10:1 prism beam expander before the grating decreases the output linewidth to less than one wavenumber over the entire tuning range. This linewidth is adequate to resolve most lines of atmospheric pollutants. If necessary, it is possible to reduce the linewidth to 0.1 wavenumbers by introducing an intracavity tilted etalon. To increase the available tunable output energy, an OPA, which was studied by Baumgartner and Byer (Reference 7), was added after the OPO source. The OPA now generates 20 millijoules output energy. However, optimization of beam overlap should increase the output energy to previously obtained values of 50 millijoules.

About 1 percent of the tunable output is reflected into a photo-acoustic cell to continuously monitor the cross-section of the observed species. The photo-acoustic cell is followed by an InSb detector, which is used as a reference detector to ratio out energy fluctuations of the OPA, and by an absorption cell to measure the absolute absorption cross-section of a pollutant at a given wavelength.

The main portion of the beam is expanded to about 3 centimeters diameter and transmitted to the telescope on the roof of the laboratory. Detection of the backscattered signal is done with a 40 centimeter, f=3 Newtonian telescope with a liquid-nitrogen-cooled InSb detector at the focal plane.

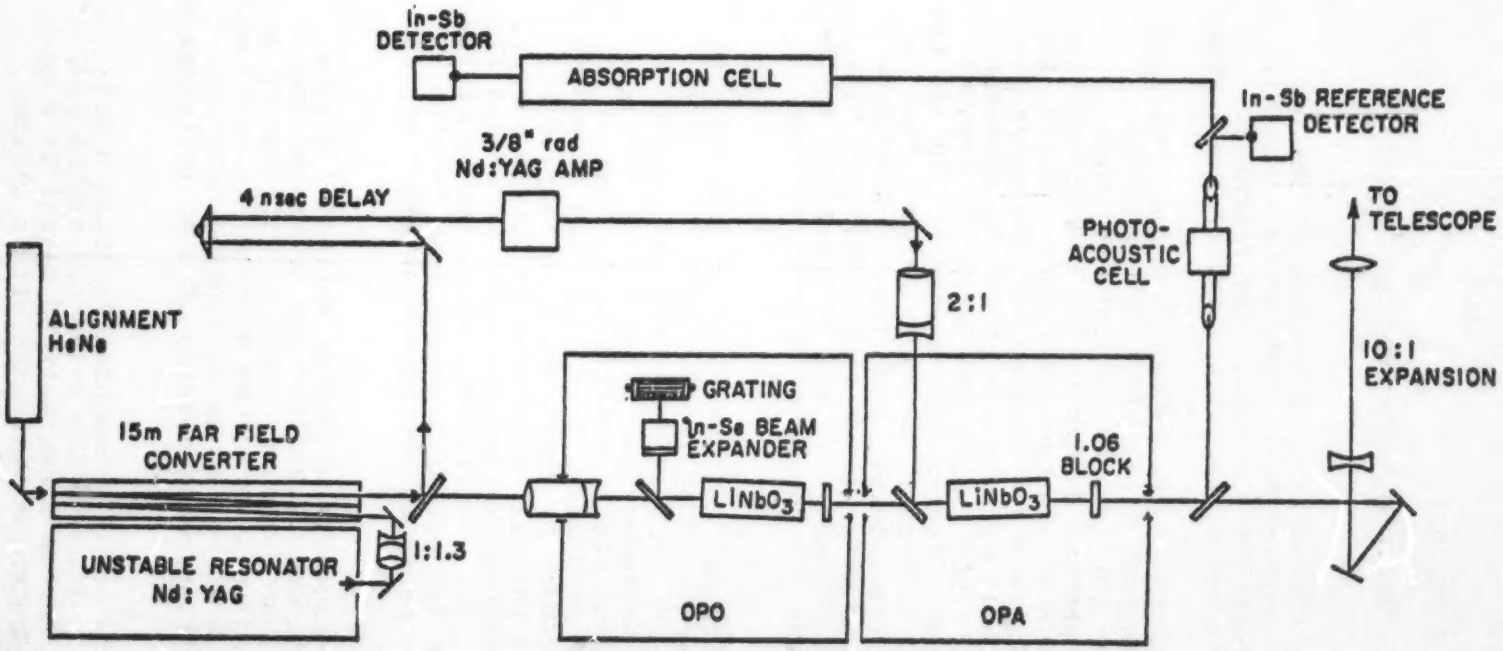

Figure 1. Schematic of the Nd:YAG laser pumped $LiNbO_3$ tunable source transmitter. The source operates at 10 pulses per second with 20 millijoules output energy tunable under computer control over a 1.4-to 4.0-micron range at 1.0 wavenumber linewidth. An etalon can be used to narrow the linewidth to less than 0.1 wavenumber.

Figure 2 shows a schematic of the improved data processing and control electronics. It is centered around the PDP/11E10 minicomputer, which uses an extensive interactive program to tune the OPO, take data, process the data, and finally display it. The signals from the cooled InSb detector and the reference detector are integrated over one shot in a gated integrator and read out by the computer which ratios and averages them. In one mode the computer tunes the OPO on and off a resonance line, uses the signal from the photo-acoustic cell to correct for slow changes of the absorption cross-section, and immediately prints the measured concentration or stores the data for laboratory processing. Another operating mode provides automatic atmospheric or in-laboratory transmittance scans over wide spectral regions. The control program greatly simplifies the handling of the system.

Important improvements were made to the remote monitoring system. The tunable source was modified by adding a prism beam expander to the OPO resonator cavity. This led to a reduction in the grating-only linewidth from 4 wavenumbers to 0.9 wavenumbers. The OPO/OPA system was enclosed in a dust-free housing and operated at a lower energy level to ensure long-term damage-free operation. Reliable operation from January 1979 to June 1979 verified that the all solid-state tunable source can be trouble-free for extended operation times.

Recently, a tilted etalon for linewidth control to 0.1 wavenumbers was installed. The galvanometer tilt control proved to have inadequate resettability and is being replaced by a stepper motor device. However, the etalon did operate over an extended 40 wavenumber scan range under computer control. When the new mechanical system is completed, atmospheric measurements can be conducted at the improved resolution.

The second area of improvement was the system control software. The software package now allows control of the tunable source, monitoring of an absorption cross-section by means of the photo-acoustic cell, normalization of the transmitted pulse energy, data collection, and processing of the returned signal. Software was also developed to display the recorded spectrum in real time or to calculate and plot the measured pollutant concentration.

Figure 2 shows a schematic of the detection system and indicates the signal processing steps. The received signal $S(\nu_1)$ and reference signal $R(\nu_1)$ and the rms deviation of the normalized signal are calculated along with the quantity $A = \log [S(\nu_1) / S(\nu_2)]$ which is proportional to the product $N \sigma L$ where N is the pollutant density, σ is the cross-section, and L is the path. Typically 20 shots on resonance and 20 shots off resonance are processed and stored. Thus, one measurement takes 4 seconds. Further signal processing and averaging is done later with the stored values A and the rms variation of A.

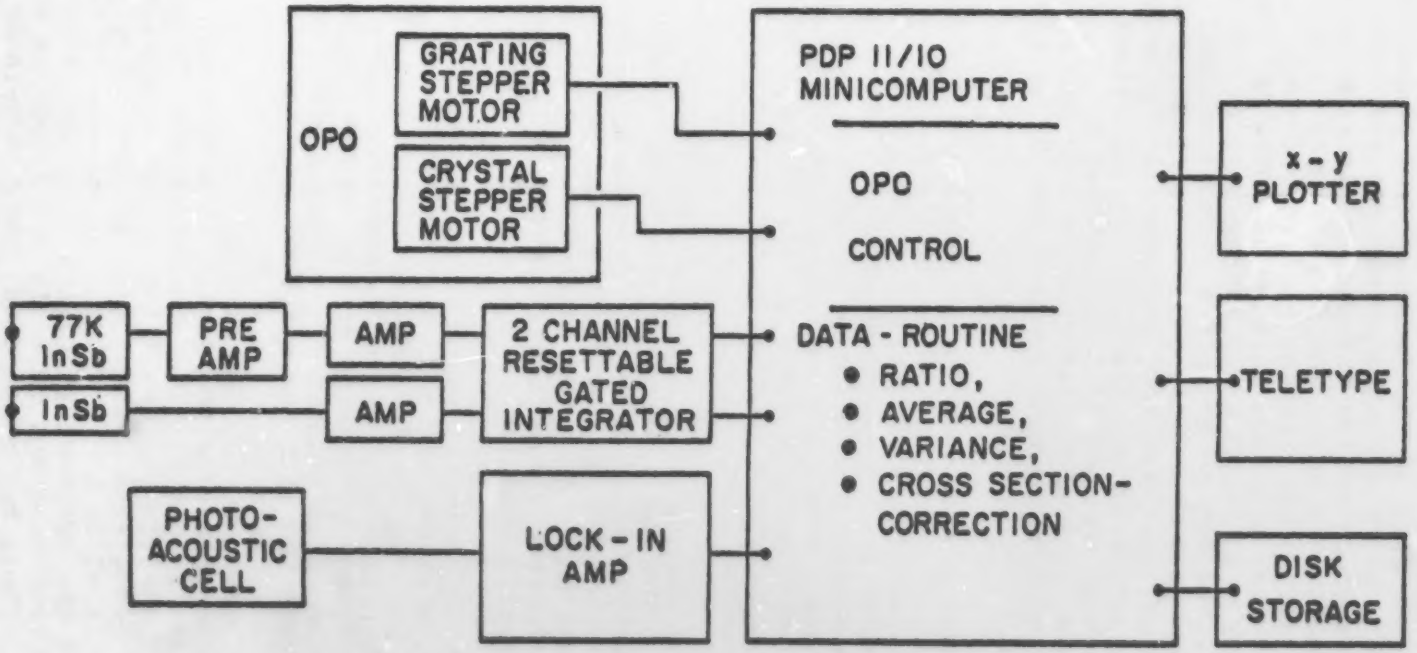

Figure 2. Schematic of the electronic control and data processing system based on the PDP11 minicomputer.

SECTION III

MEASUREMENTS

Using the tunable OPO/OPA source, single ended atmospheric absorption measurements were made. The typical path length was 1.54 kilometers, using the Hoover Tower structure as the topographical target. Spectral scans over a wavelength range from 1.45 to 4.0 microns have been made.

Figure 3 shows a section of a spectral scan in the 5500 to 5800 wavenumbers range. The 300 wavenumber scan is a part of a scan that extends to 2500 wavenumbers. The region shown in Figure 3 covers the overtone absorption band of H_2O. The absorption peaks are not noise but are individual absorption lines of water vapor. To illustrate the resolution of the source, Figure 4 shows a section of water vapor absorption over a 40 wavenumber interval. In this scan the water vapor lines have been labeled. The scan has a resolution near 1 wavenumber and, therefore, does not resolve the water vapor lines which have half-widths near 0.03 to 0.1 wavenumbers. However, water vapor density can be determined with the 1 wavenumber resolution if an effective absorption cross-section is used.

Figure 5 shows a segment of the atmospheric absorption spectrum near the methane 3.4-micron fundamental band. Both CH_4 and H_2O absorption lines are present. To clearly identify the CH_4 lines and to aid in selecting a transition free from water vapor, an absorption spectrum of CH_4 was taken in the laboratory. A section of the scan centered on the P-branch is shown in Figure 6. Figures 5 and 6 can be overlaid to show that the P10 methane transition is of proper strength and nearly water vapor free for atmospheric measurement over the 1.5 kilometer path.

The ability to select interference-free absorption bands and to verify the location of spectral lines by scanning the spectrum is a major advantage of the tunable source.

The P10 transition was selected for CH_4 measurements. The computer was programmed to tune onto the P10 line and off the line every 20 pulses. The data was normalized, ratioed, and processed to show ppm CH_4. An effective cross-section for CH_4 (P10) was utilized based on the resolution of the OPO/OPA source. To correct for any long-term drift, the cross-section was continuously measured during a run by a photo-acoustic detector cell. The value of the cross-section was used to calculate the methane concentration in near real time.

Figure 7 shows a segment of an 18-hour CH_4 measurement run. Here the raw measurements are shown for 20 shots/line averaging

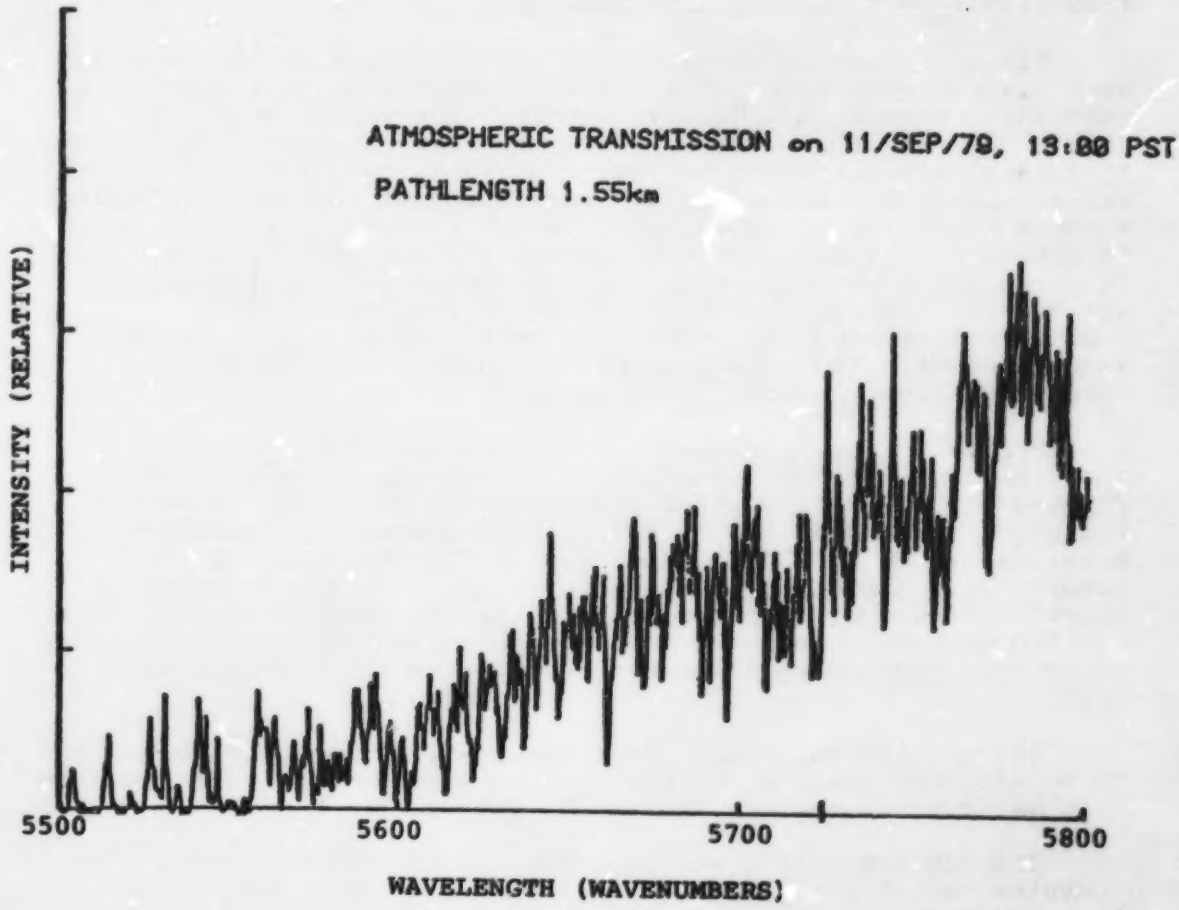

Figure 3. A segment of an atmospheric transmission scan over a 1.55-kilometer path in the spectral range from 5500 to 5800 wavenumbers.

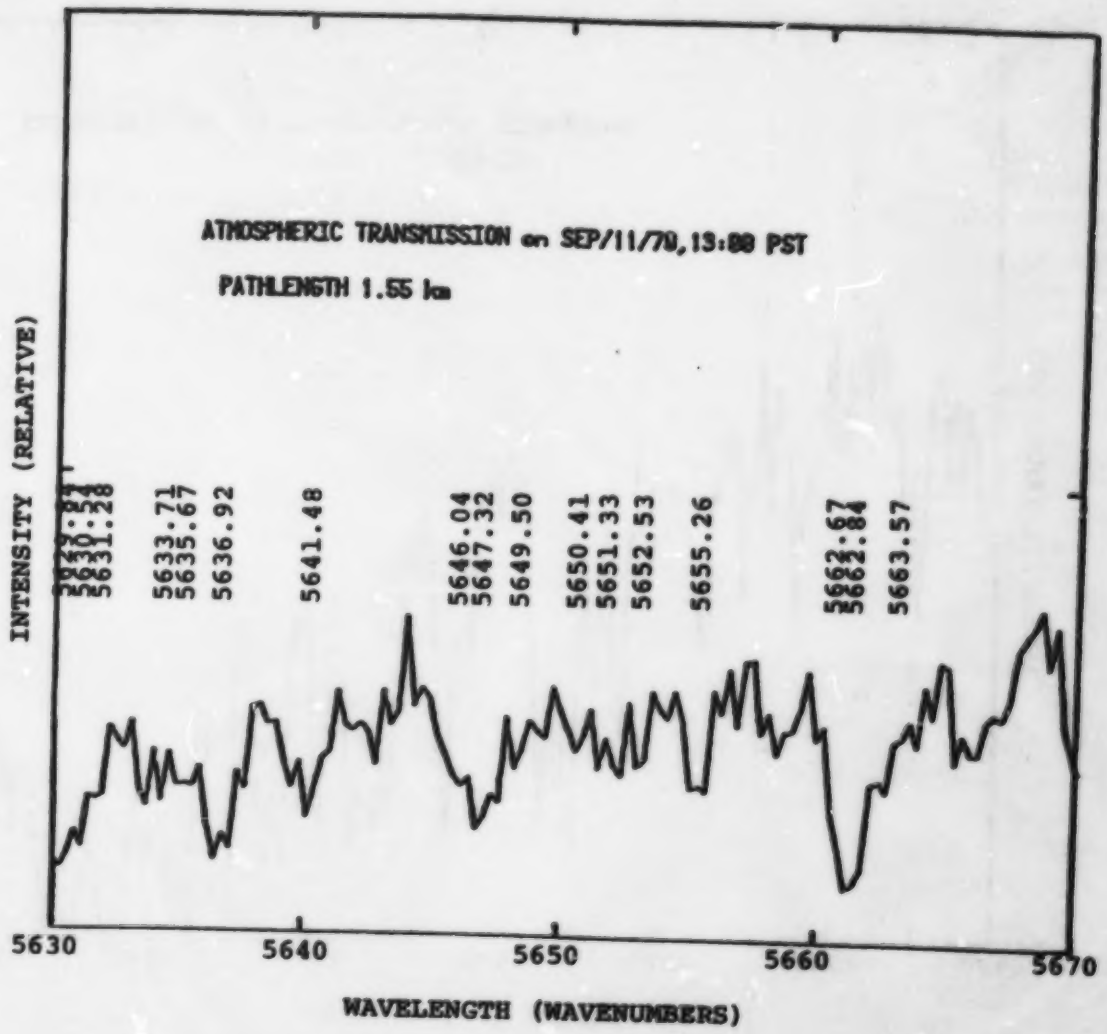

Figure 4. A detailed segment of the scan shown in Figure 3. Here a region of H_2O absorption is shown in which H_2O lines have been identified and labeled.

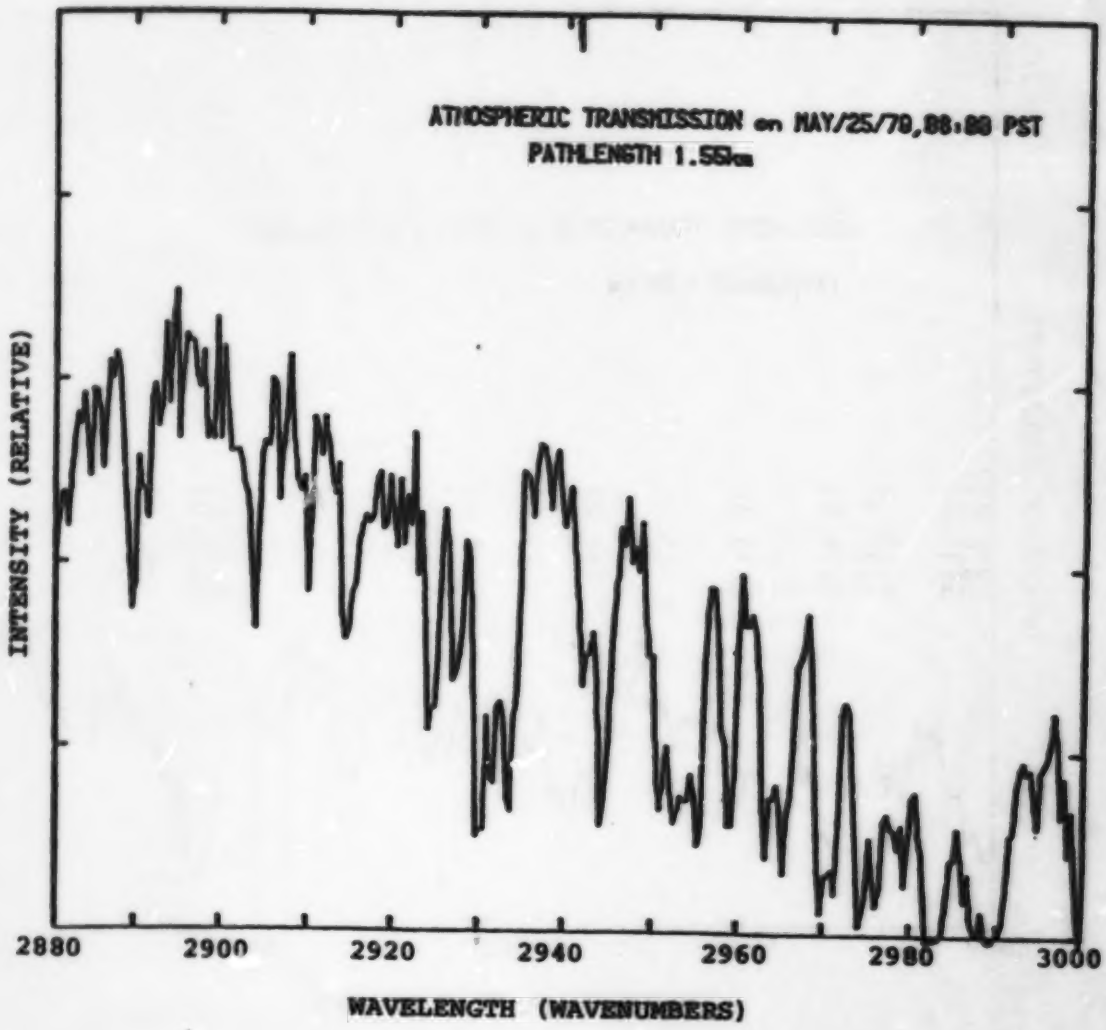

Figure 5. A segment of an atmospheric absorption scan near the CH_4 fundamental absorption band at 3.4 microns.

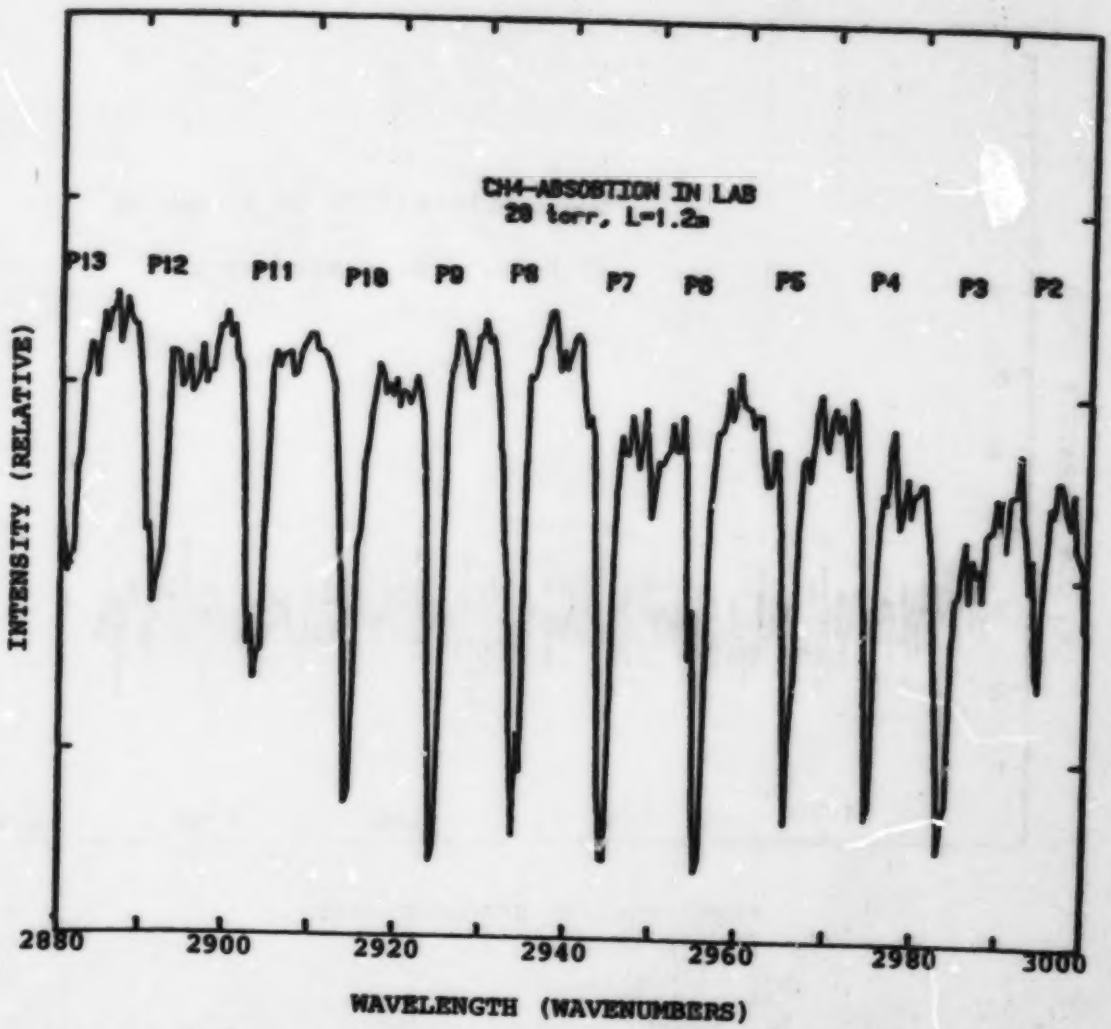

Figure 6. An in-laboratory CH_4 absorption spectrum of the identical spectral region shown in Figure 5. Figure 6 can be overlaid onto Figure 5 to show the CH_4 absorption peaks and to help select water vapor-free CH_4 absorption lines.

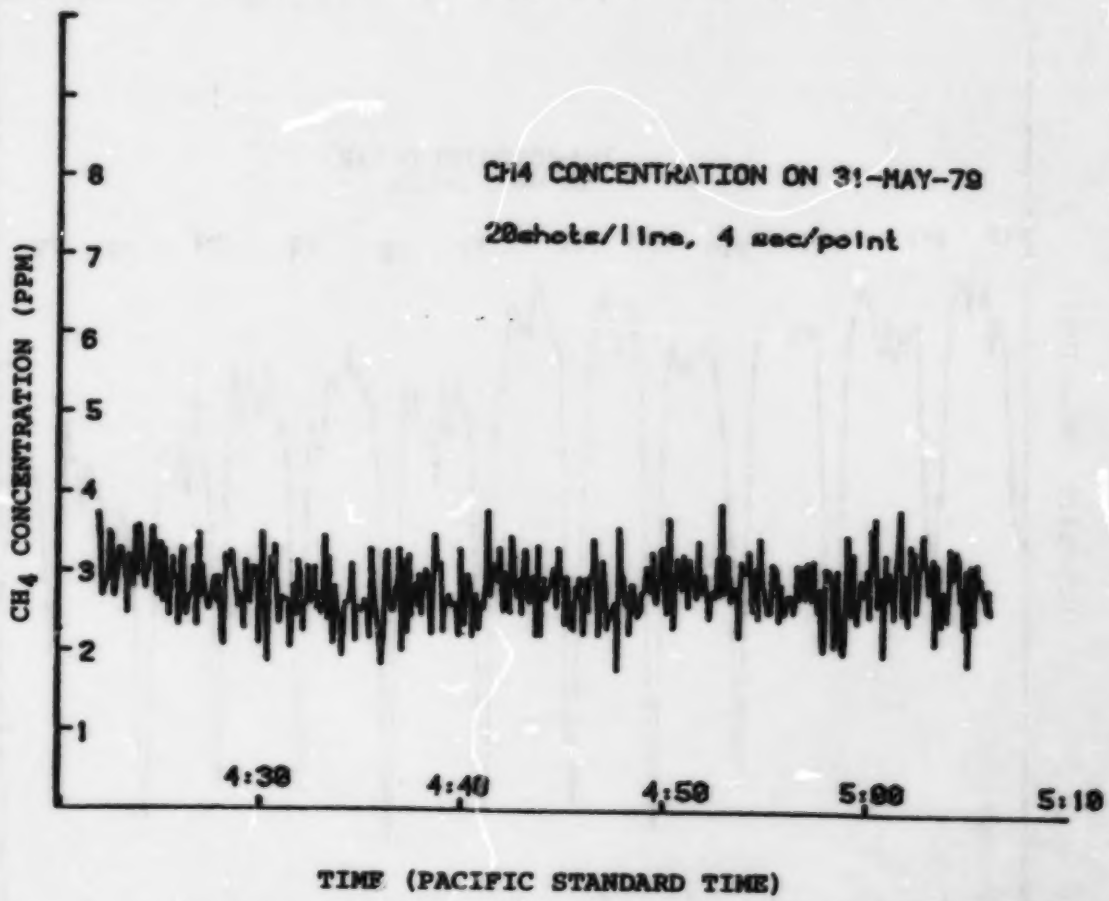

Figure 7. A section of an 18-hour measurement of CH_4 on 31 May 1979 over a 1.55 kilometer path. The 20-shot average yields a 4-second measurement time and a 0.6-ppm rms error.

or 4 seconds per point. The rms fluctuations are calculated to be 0.6 parts per million. To improve the precision of the measurement longer averaging times can be used. Figure 8 shows a section of the same CH_4 measurement run with an 80-second averaging time. Here the rms deviation is reduced to 0.03 ppm which is less than the CH_4 fluctuation level in the atmosphere.

During these measurements there was concern that the measured CH_4 levels were too high since the global average CH_4 level is near 1.5 ppm. Therefore, hourly CH_4 measurements were obtained from the Redwood City Bay Area Pollution Control District point monitoring station.

Figure 9 shows the measurements at Stanford over a 10-hour period and the hourly averaged measurements from the monitoring station which is located 8 kilometers north of Stanford. The agreement is excellent and is within the variations of CH_4 in the atmosphere. On the night of 30 May 1979 the weather was clear with a very light wind. The anomalously high CH_4 levels observed in the south bay area may be due to the large biomass production rate from marshes and city dumps located along the bay itself.

To check further on the correlation between our measurements and the station measurements, a second CH_4 run was made on 6 and 7 June 1979. Figure 10 shows the results and comparison. In this case the wind was blowing down the bay from Redwood City toward Stanford. The wind velocity and distance gave a 20 to 30-minute delay time from Redwood City to Stanford. This delay time is in good agreement with the peak CH_4 measurement at 22.00 at Redwood City which was observed at Stanford at 22.30. Later in the evening the wind ceased, making the measurements independent of the Redwood station.

It should be noted that the LIDAR system was making CH_4 measurements every 50 seconds. The Redwood City flame ionization detector measurements are averaged over 1-hour intervals for recording. Even though the measurement systems are separated physically, the agreement in measured CH_4 levels is excellent as should be expected in a region free of large sources of CH_4 in the area between Stanford and Redwood City.

During the final phase of this program the H_2O spectrum was investigated to determine optimal wavelengths for density and temperature measurements. Figure 11 shows a section of the H_2O absorption spectrum near 5650 wavenumbers. The labeled peaks have been selected for atmospheric temperature measurements due to their close proximity in wavenumber and their widely spaced lower levels. Here E_o denotes the energy above the H_2O ground state in wavenumbers.

These two H_2O lines should allow temperature measurements to better than 1°C for a 1 percent precision in absorption

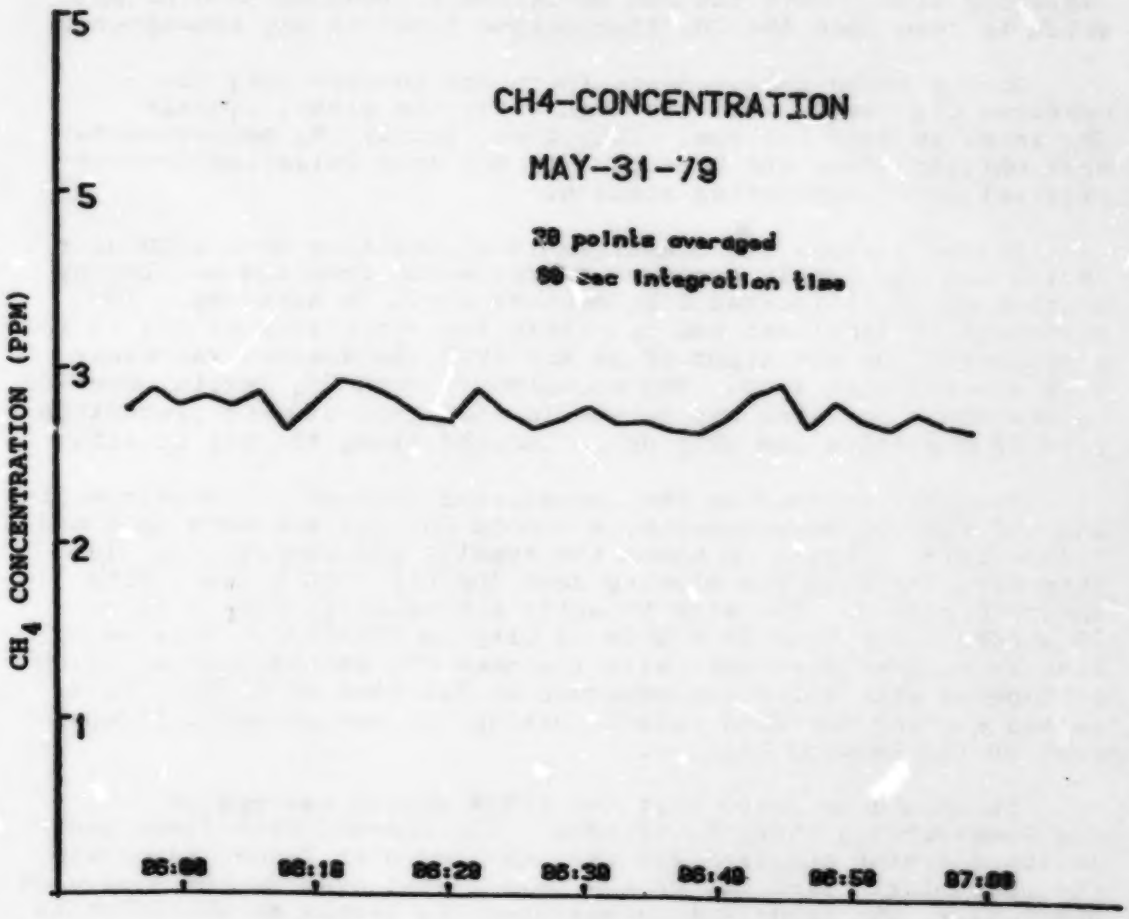

Figure 8. A part of the CH_4 measurement showing CH_4 fluctuations over the path being monitored. The statistical rms noise of the measurement is 0.03 ppm which is less than the CH_4 fluctuation level.

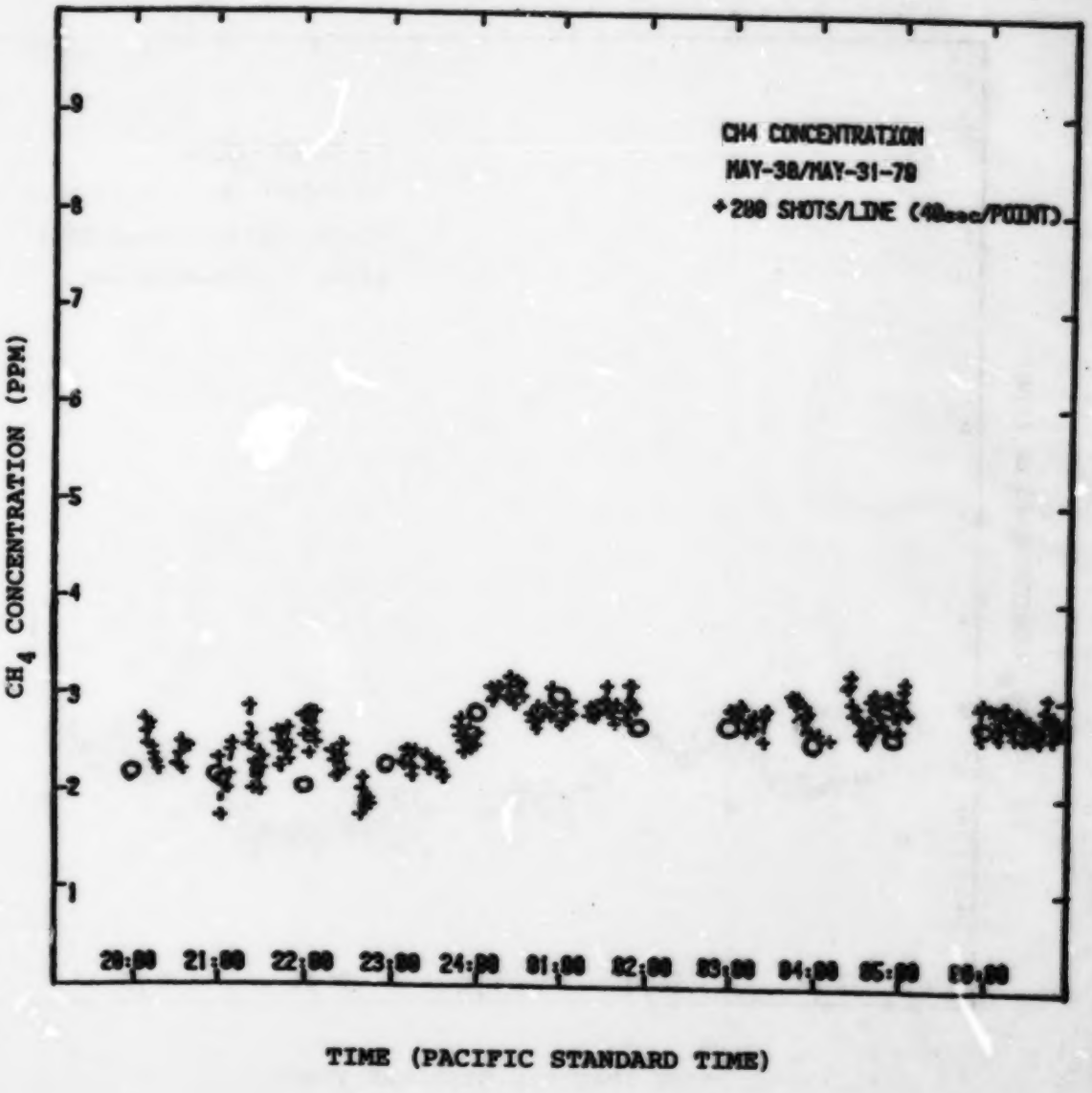

Figure 9. CH_4 ppm versus time over a 12-hour period. The Stanford LIDAR data is plotted as crosses. The point-monitoring hourly-averaged CH_4 levels are shown as open circles.

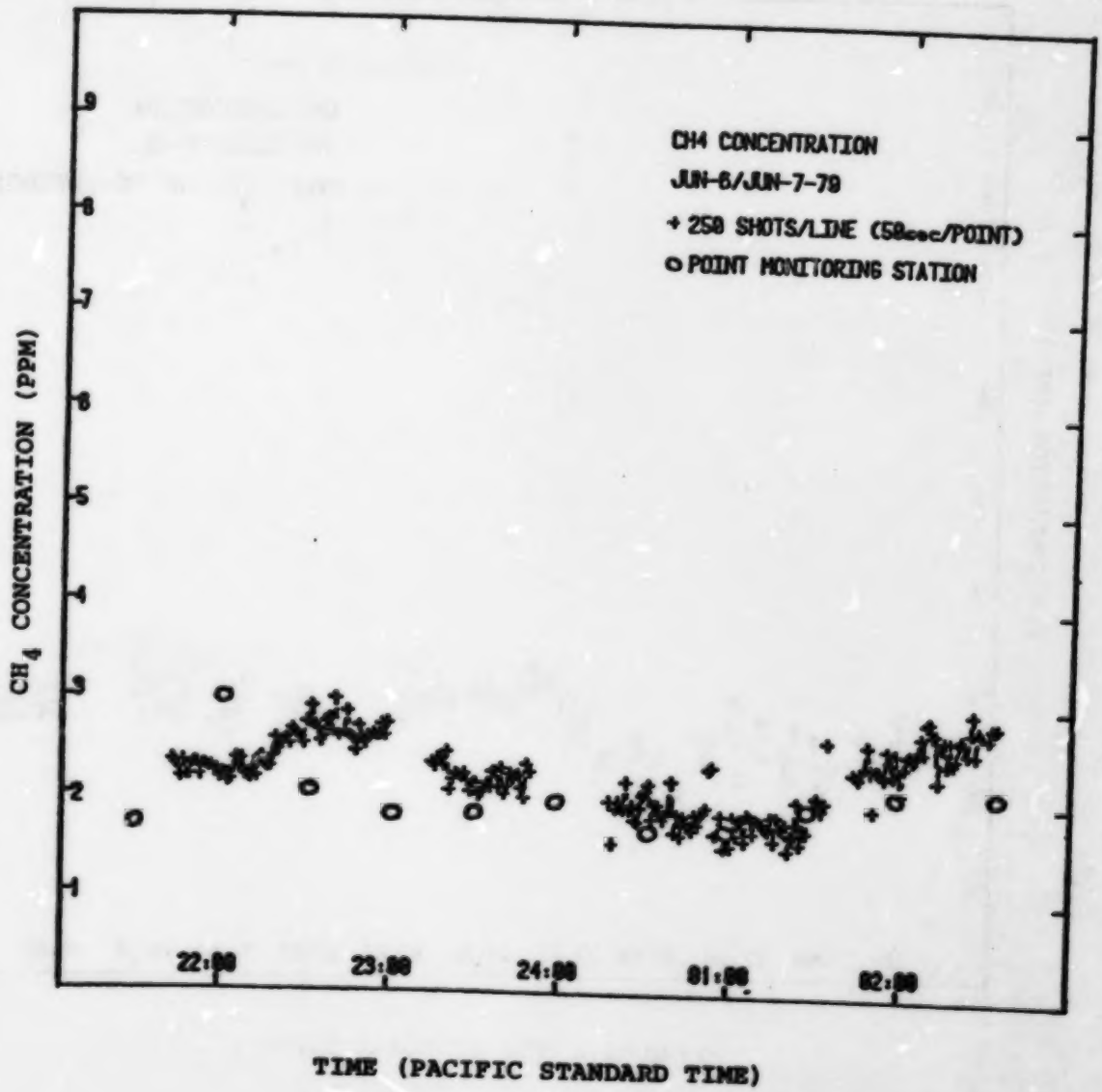

Figure 10. CH_4 ppm versus time for a second measurement run. The Stanford LIDAR data is plotted as crosses. Here a prevailing wind yielded a 30-minute delay between the atmosphere at Redwood City point monitoring station and its arrival near Stanford campus.

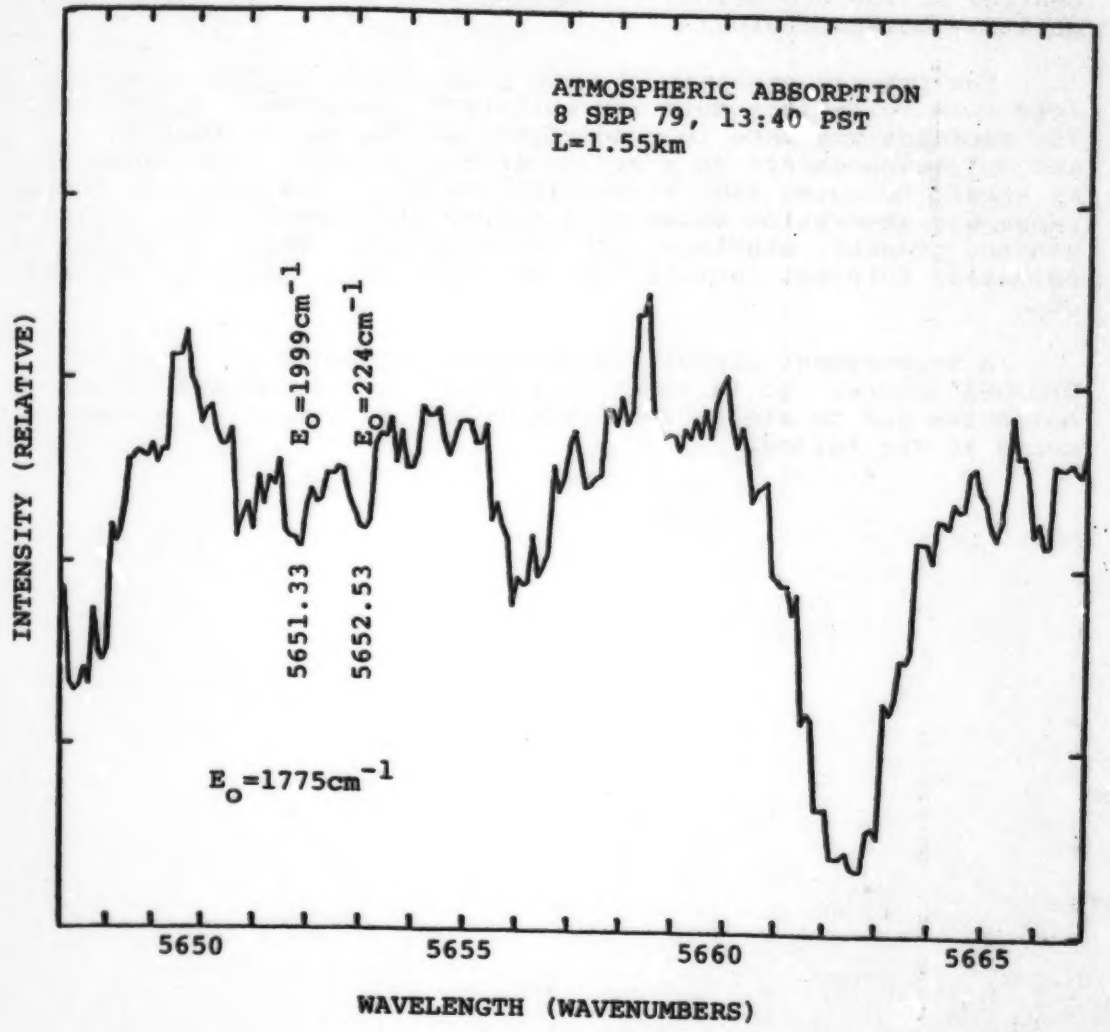

Figure 11. A section of the H_2O atmospheric absorption spectrum of use for H_2O and atmospheric temperature measurements.

measurement. The CH_4 measurements show that such a measurement precision is possible for an averaging time of approximately 5 minutes. Preliminary measurements have shown that the peak ratios of the two H_2O lines do vary with atmospheric temperature as expected. Improvements are being made to the linewidth control of the OPO before attempting long-term atmospheric temperature measurements.

The primary emphasis of this program was to demonstrate long-term reliable remote air pollution measurement capability. The decision was made to concentrate on CH_4 rather than to attempt measurements on a wider variety of molecules. However, it should be noted that within the OPO 1.4- to 4.0-micron tuning range are absorption bands of a number of hydrocarbons, including ethane, propane, ethylene, and formaldehyde. Other molecules of potential interest include HCl, HF, N_2O, NO_2, H_2S, NH_3, CO, and CO_2.

A measurement capability has been demonstrated using an OPO/OPA source. It is hoped to extend these results to other molecules and to atmospheric meteorological parameter measurements in the future.

SECTION IV

CONCLUSIONS

The reliable use of an OPO-based remote air pollution system has been demonstrated. Fully automatic operation of this system is possible. Future measurements will demonstrate the capability to measure many pollutants with the same system, thus showing another advantage of the tunability. The advantages of the continuous tunability for cross-section optimization and interference avoidance have been clearly demonstrated. The possibility of improving the measurement accuracy by appropriate signal averaging has also been demonstrated. Finally, long-term operation under full computer control of the all solid-state laser source and $LiNbO_3$ OPO/OPA tunable source has demonstrated the potential for future use in remote atmospheric measurements.

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